

# The role of adsorption of sodium bis(2-ethylhexyl) sulfosuccinate in wetting of glass and poly(methyl methacrylate) surface

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## Abstract

Advancing contact angles,  $\theta$ , for aqueous solutions of the anionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were measured on glass and poly(methyl methacrylate) (PMMA) surface. Using the obtained results we determined the properties of aqueous AOT solutions in wetting of these surfaces. It occurs that the wettability of glass and PMMA by these solutions depends on the concentration of AOT in solution. There is almost linear dependence between the contact angle ( $\theta$ ) and concentration of AOT ( $\log C$ ) in the range from  $5 \times 10^{-4}$  to  $2.5 \times 10^{-3}$  M/dm<sup>3</sup> (value of the critical micelle concentration of AOT—CMC) both for glass and PMMA surface. For calculations of AOT adsorption at solid (glass, PMMA)–solution drop–air system interfaces the relationship between the adhesion tension ( $\gamma_{LV} \cos \theta$ ) and surface tension ( $\gamma_{LV}$ ) and the Gibbs and Young equations were taken into account. From the measurement and calculation results the slope of the  $\gamma_{LV} \cos \theta - \gamma_{LV}$  curve was found to be constant and equal 0.7 for glass and  $-0.1$  for PMMA over the whole range of AOT concentration in solution. From this fact it can be concluded that if  $\Gamma_{SV}$  is equal zero then  $\Gamma_{SL} > 0$  for the PMMA–solution and  $\Gamma_{SL} < 0$  for glass–solution systems. It means that surfactant concentration excess at PMMA–solution interface is considerably lower than at solution–air interface, but this excess of AOT concentration at glass–solution interface is lower than in the bulk phase. By extrapolating the linear dependence between the adhesion and surface tension the value of the critical surface tension ( $\gamma_c$ ) of wetting for glass and PMMA was also determined, that equaled 25.9 and 25.6 mN/m for glass and PMMA, respectively. Using the value of the glass and PMMA surface tension as well as the measured surface tension of aqueous AOT solutions in Young equation, the solid–liquid interface tension ( $\gamma_{SL}$ ) was found. There was a linear dependence between the  $\gamma_{SL}$  and  $\gamma_{LV}$  both for glass and PMMA, but there were different slope values of the curves for glass and PMMA, i.e.  $-0.7$  and  $0.1$ , respectively. The dependence between the work of adhesion ( $W_A$ ) and surface tension ( $\gamma_{LV}$ ) was also linear of different slopes for glass and for PMMA surface.

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## 1. Introduction

Surfactant adsorption is a transfer process of surfactant molecules from a bulk solution phase to the surface or interface. Adsorption of surfactants at solid–liquid interface systems plays a very important role in technological and industrial applications such as printing, detergency, cosmetics, mineral flotation, dispersion and others [1].

Adsorption of surfactants at polar solid–water interface is a complex process. A driving force of adsorption of surfactants is

a combination of electrostatic and chemical interactions, lateral chain–chain associative interactions, hydrogen bonding and solvation of adsorbate species [2].

From the practical point of view the most interesting systems are those including water or different aqueous solutions. In three phase hydrophobic solid–water–air systems, surface active agents, for example surfactants, adsorb at water–air and solid–water interfaces reducing the water surface tension and solid–water interface tension to values which can cause contact angle decrease [3,4]; however, in systems including hydrophilic solids the adsorption of surfactants at solid–water interface can decrease or increase or not change the solid–water interface tension [4]. Contact angle changes are sometimes difficult to predict. The solid–liquid interface tension can, among other

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things, be determined from the Young equation by measuring the contact angle [4,5]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

This and Gibbs equation [4] were taken into account by Lucassen-Reynolds [6] to analyze the adsorption of a surfactant at solid–air, liquid–air and solid–liquid interfaces. Using the Lucassen-Reynders [6] equation it was found that for completely nonpolar surfaces, for example polytetrafluoroethylene (PTFE), the  $\Gamma_{SL}$  and  $\Gamma_{LV}$  were the same because the slope of the line representing the relationship between  $\gamma_{LV} \cos \theta$  and  $\gamma_{LV}$  was equal  $-1$ . It indicates that adsorption at solid–liquid and liquid–air interface is the same [4]. In the case of polar solids the slope of  $\gamma_{LV} \cos \theta$  versus  $\gamma_{LV}$  curve differs significantly from  $-1$  [4,7]. It results from the fact that adsorption of surfactants at solid–liquid interface is different than at liquid–air interface.

Because the wettability of solids by aqueous solution of surfactants and their adsorption at water–air and solid–water interface are strongly related, and adsorption of oppositely charged surfactants and surfaces is not completely explained, we tried to determine the adsorption properties of aqueous AOT solutions at water–air, glass–water and PMMA–water interfaces in regard to glass and PMMA wettability by surfactant solutions.

For this purpose measurements of the contact angle of aqueous AOT solutions on glass and PMMA surface were made in the range of the surfactant concentration from 0 to  $10^{-2}$  M/dm<sup>3</sup>, and the obtained results were analyzed by using the Lucassen-Reynders equation [6].

## 2. Experimental

### 2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate ( $C_{20}H_{37}NaO_7S$ ) (AOT, Fig. 1) (Sigma–Aldrich), (purity  $\geq 99\%$ ) was used for aqueous solution preparation. For preparation of AOT aqueous solutions doubly distilled and deionized water (Destamat Bi 18E) was used. The surface tension of water ( $\gamma_w = 72.8$  mN/m) was always controlled at 293 K by Krüss K9 tensiometer under atmospheric pressure by the ring method before the solutions were prepared.

Poly(methyl methacrylate) plates (Z. Ch. Oświęcim, Poland) were cut from a large sheet, one side of which was covered with paper. Microscope glass slides were also used in the measurements. The cleaning procedure in the case of glass

was the same as in the case of the poly(methyl methacrylate) plates. The poly(methyl methacrylate) and glass plates were cleaned in ultrasonic bath in doubly distilled water for 20 min [8]. Then the plates were dried by blowing hot air and next kept at room temperature in a desiccator filled with a dehydrating agent. The quality of the surface of each plate was controlled by a polarizing microscope (Nikon, ECLIPSE E600 POL). Plates of a good smoothness were used for the contact angle measurements.

### 2.2. Contact angle measurements

Advancing contact angles for water and aqueous solutions of AOT at a given concentration on PMMA and glass plates were measured by the sessile drop method using the telescope – goniometer system at  $25 \times$  magnification in a thermostated measuring chamber at  $20 \pm 0.1$  K. After settling a drop of aqueous solution of the surfactant on a PMMA or glass plate the contact angle was read immediately on both sides of the drop. The measurements were repeated several times by settling other drops on the same plate. Next, a new plate was placed in the chamber and the above procedure was repeated. The reported contact angle values were the average of at least 10 independent drops, and they were exactly reproducible to  $1.1^\circ$ .

## 3. Results and discussion

### 3.1. Wetting of glass and PMMA surfaces

In general wetting is a displacement of one fluid by another from the surface, but this term is commonly applied to the displacement of air from a solid surface by water or an aqueous solution. Three types of wetting have been distinguished: (a) spreading wetting, (b) adhesional wetting, (c) immersional wetting [4,5]. For all the three types of wetting, reduction of the interfacial tension between solid and wetting liquid ( $\gamma_{SL}$ ) is beneficial in contrast to reduction of the  $\gamma_{LV}$  which is not always advantageous [4].

The obtained contact angle values on the given solids are shown in Fig. 2: glass (curve 1), PMMA (curve 2). The relationship between the surface tension and AOT aqueous solution concentration was presented in our previous work [3].

For glass the contact angle values change from  $40^\circ$  to  $16^\circ$ , and for PMMA from  $75^\circ$  to  $30^\circ$ . From this figure is also seen that in the  $\log C$  range from  $-7$  to  $-5$  the  $\theta$  values are slightly changed both for glass and PMMA surface. A considerable decrease of  $\theta$  as a function of  $\log C$  is observed when AOT

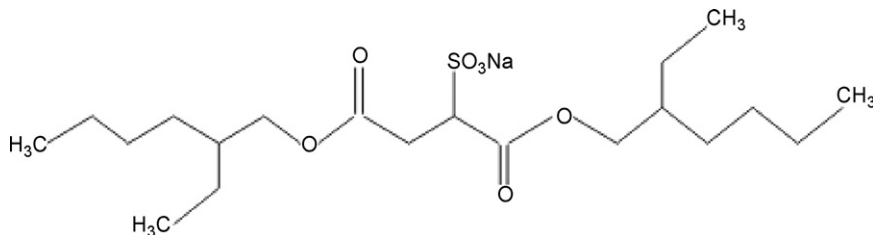


Fig. 1. A structure of AOT molecule.

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